

W. Robert Scheidt\* and Bruce C. Noll

University of Notre Dame, Department of Chemistry and Biochemistry, 251 Nieuwland Science Hall, Notre Dame, IN 46556-5670, USA

Correspondence e-mail: w.r.scheidt.1@nd.edu

## Key indicators

Single-crystal X-ray study  
T = 100 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$   
Disorder in solvent or counterion  
R factor = 0.036  
wR factor = 0.108  
Data-to-parameter ratio = 19.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

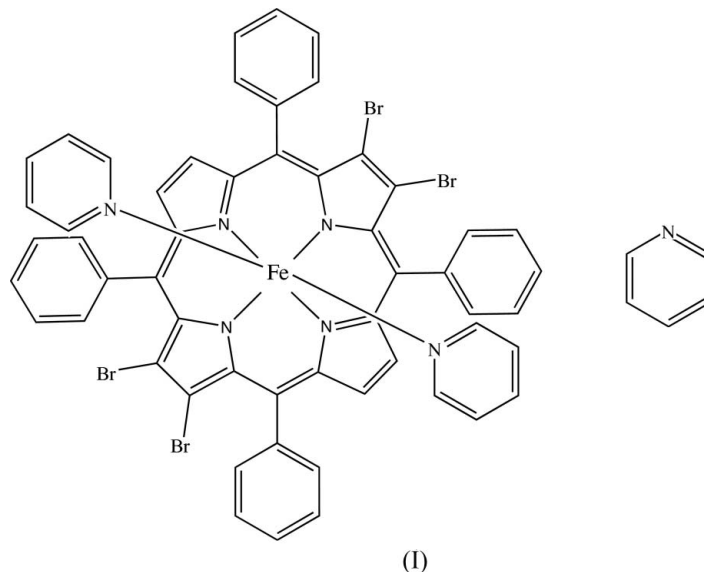
## Dipyridine(2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin)iron(II) pyridine solvate

Received 7 July 2006  
Accepted 13 July 2006

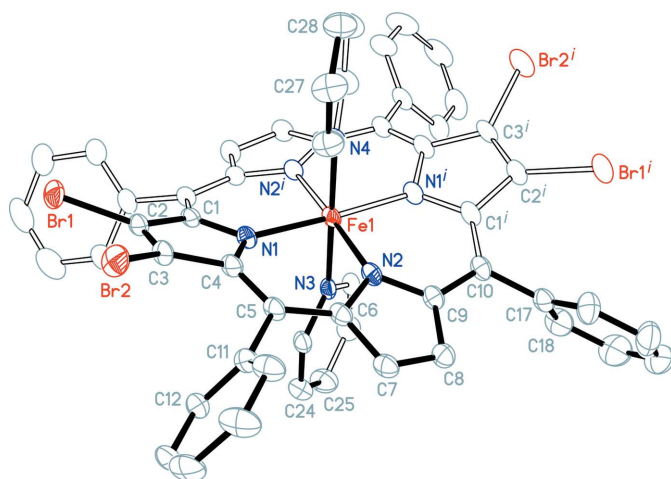
The complex molecule of the title compound,  $[\text{Fe}(\text{C}_{44}\text{H}_{24}\text{Br}_4\text{N}_4)(\text{C}_5\text{H}_5\text{N})_2] \cdot \text{C}_5\text{H}_5\text{N}$ , is located on a twofold axis that passes through the Fe atom and the pyridine ligands. Only slight asymmetry, *viz.* 0.010 Å elongation due to the Br substituents, is seen in the Fe–N<sub>porph</sub> distances. The pyridine ligands are twisted by 19.18 (13)° from each other. The uncoordinated pyridine molecule is disordered over an inversion center.

## Comment

The title compound,  $[\text{Fe}(\text{TPPBr}_4)(\text{py})_2] \cdot \text{py}$ , (I), is a low-spin bis(pyridine)iron(II) complex that was studied as part of a program investigating ways to achieve control of axial ligand orientation in iron porphyrin derivatives (Safo *et al.*, 1991). Two effects are possible with this porphyrin ligand: the effect from the four  $\beta$ -pyrrole electron-withdrawing substituents and the possible conformational effects of the peripherally crowded but asymmetrically substituted porphyrin.

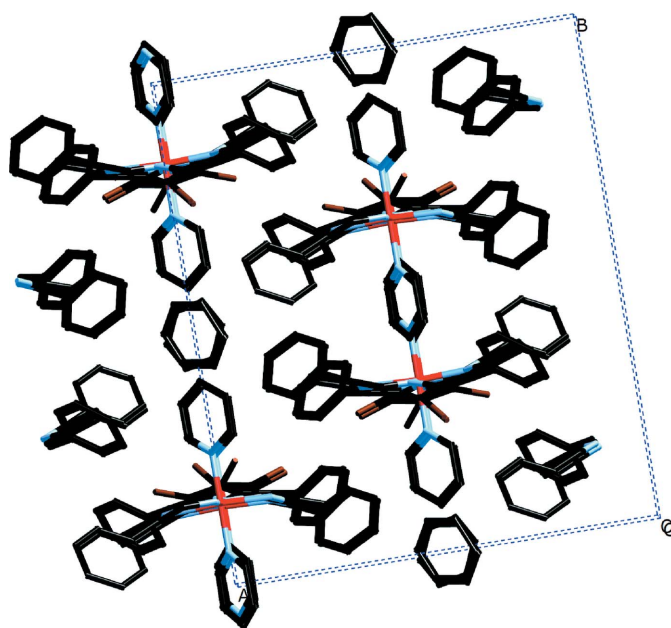


The molecular structure of (I) is shown in Fig. 1. The core asymmetry is very small, with Fe–N<sub>por</sub> bond distances of 1.971 (2) and 1.981 (2) Å, with only a very small elongation caused by the Br substituents. This is very much less than in some derivatives. For example, two different crystalline forms of high-spin  $[\text{Fe}(\text{TPPBr}_4)_2\text{O}]$  (Kadish *et al.*, 1997; Li *et al.*, 2000) have Fe–N<sub>por</sub> bond distances that differ by more than 0.05 Å. A similar, even larger, difference is seen in  $[\text{Zn}(\text{TPPBr}_4)]$  (Zou *et al.*, 1997). However, small differences (1.90 and 1.91 Å) are also seen in  $[\text{Ni}(\text{TPPBr}_4)]$  (Zou *et al.*,



**Figure 1**

The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. The unique part of the molecule is drawn with solid bonds. H atoms and the solvent molecule have been omitted for clarity. C atoms of the phenyl rings are numbered sequentially. [Symmetry code: (i)  $-x, y, -z + \frac{1}{2}$ ]



**Figure 2**

A view of the crystal packing, perpendicular to (001).

1994) and in two crystalline forms of  $[\text{Fe}(\text{TPPBr}_4)(\text{NO})]$  (Scheidt *et al.*, 2000), suggesting that the magnitude of the asymmetry in the porphyrin hole is related to the natural bond lengths and strength of the bonds. The average 1.976 (7) Å bond length is at the very low end of distances observed for low-spin iron(II) (Scheidt, 2000).

The small size of the central hole is the result, at least in part, of the core conformation in (I). The core is substantially distorted from planarity by a combination of both ruffling and saddling. The deformation shows asymmetry because of the two types of pyrrole rings, leading to overall core symmetry of  $C_2$  and not  $S_4$ . Unlike the case of  $[\text{Fe}(\text{TFPPBr}_8)(\text{py})_2]$ , where

the strongly saddled core leads to a near perpendicular orientation of the two axial pyridine ligand planes (Grinstaff *et al.*, 1995), the core of (I) appears to have little effect on the orientation of the two pyridine planes: the angle between them is 19.18 (13)°. It has been noted previously that coplanar axial ligands are typically seen in iron(II) porphyrin systems (Safo *et al.*, 1997). The axial Fe–N<sub>py</sub> bond distances of 2.000 (3) and 2.040 (3) Å are within the normal range observed.

Examination of the crystal packing of (I) (Fig. 2) shows the uncoordinated pyridine to be disordered over an inversion center in a channel perpendicular to (001). The porphyrins pack in pairs of chains also perpendicular to (001) and alternating concave up and concave down along the chains.

## Experimental

The  $\beta$ -pyrrole-substituted tetrabromotetraphenylporphyrin derivative ( $\text{H}_2\text{TPPBr}_4$ ) was synthesized following the reported method of Callot (1974). The perchlorato- and chloroiron(III) derivatives were prepared by modified literature methods (Alder *et al.*, 1970; Buchler, 1975; Dolphin *et al.*, 1977). The bis(pyridine) ligated iron complex was prepared by stirring the perchlorate derivative (50 mg) with pyridine (2 ml) under argon for 1 h. Single crystals of (I) were obtained by liquid diffusion of hexane into a  $\text{CH}_2\text{Cl}_2$  solution. The crystals exhibit Fe in the +2 oxidation state (UV–vis  $\lambda_{\text{max}} = 436, 540, 576 \text{ nm}$ ).

### Crystal data

$[\text{Fe}(\text{C}_{44}\text{H}_{24}\text{Br}_4\text{N}_4)(\text{C}_5\text{H}_5\text{N})_2] \cdot \text{C}_5\text{H}_5\text{N}$	$Z = 4$
$M_r = 1221.46$	$D_x = 1.674 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 18.4633 (5) \text{ \AA}$	$\mu = 3.66 \text{ mm}^{-1}$
$b = 19.9786 (6) \text{ \AA}$	$T = 100 (2) \text{ K}$
$c = 14.4636 (4) \text{ \AA}$	Block, dark red
$\beta = 114.688 (1)^\circ$	$0.15 \times 0.11 \times 0.11 \text{ mm}$
$V = 4847.5 (2) \text{ \AA}^3$	

### Data collection

Bruker X8 APEXII CCD area-detector diffractometer	51139 measured reflections
$\varphi$ and $\omega$ scans	6171 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)	4952 reflections with $I > 2\sigma(I)$
$T_{\text{min}} = 0.60, T_{\text{max}} = 0.67$	$R_{\text{int}} = 0.039$
	$\theta_{\text{max}} = 28.6^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 9.6451P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.10$	$\Delta\rho_{\text{max}} = 1.03 \text{ e \AA}^{-3}$
6171 reflections	$\Delta\rho_{\text{min}} = -1.02 \text{ e \AA}^{-3}$
323 parameters	
H-atom parameters constrained	

The molecule of pyridine cocrystallized with the porphyrin is located about an inversion center at  $(0, \frac{1}{2}, \frac{1}{2})$ . The N position in this pyridine molecule could not be determined due to the crystallographically imposed disorder. Thus, all pyridine atoms were refined as C and the three associated unique H atoms were included at 0.8333 occupancy. Due to the disorder of the N position in the pyridine, the average C–C distance is shorter than normal. All H atoms were

refined using a riding model, with C–H distances of 0.95 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* and *SAINT* (Bruker, 2004); data reduction: *SAINT* and *XPREP* (Sheldrick, 2003); program(s) used to solve structure: *XS* (Sheldrick, 2001); program(s) used to refine structure: *XL* (Sheldrick, 2001); molecular graphics: *XP* (Sheldrick, 1998); software used to prepare material for publication: *XL* and *enCIFer* (Allen *et al.*, 2004).

The authors thank the US NIH (grant No. GM-38401) and NSF (grant No. CHE-0443233) for support.

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